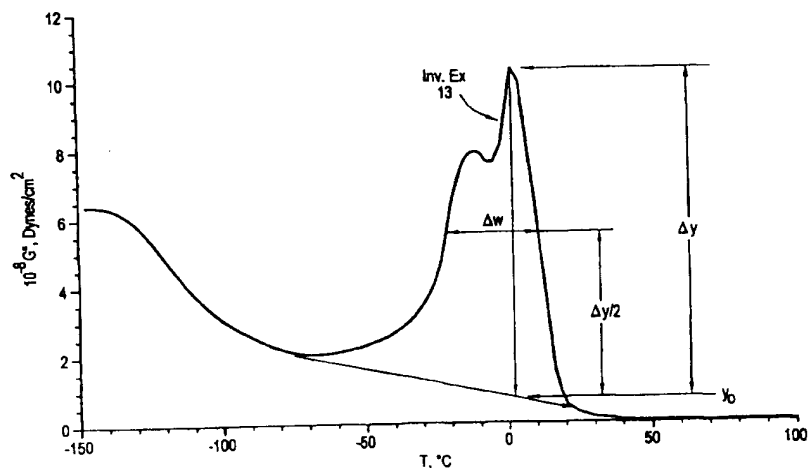




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(21) International Application Number: PCT/US00/04121 (22) International Filing Date: 17 February 2000 (17.02.00) (30) Priority Data: 60/120,347                      17 February 1999 (17.02.99)                      US (71) Applicant: THE DOW CHEMICAL COMPANY [US/US]; 2030 Dow Center, Midland, MI 48674 (US). (72) Inventors: CHEUNG, Yunwa, W.; 104 Rosemary Lane, Lake Jackson, TX 77566 (US). GUEST, Martin, J.; 58 Yaupon Court, Lake Jackson, TX 77566 (US). ROSEN, Robert, K.; 2639 Centenary Street, Houston, TX 77005 (US). KOLTHAMMER, Brian, W., S.; 109 Rosewood, Lake Jackson, TX 77566 (US). (74) Agent: MCKINNEY, Osborne, K.; Intellectual Property, B-1211, 2301 Brazosport Boulevard, Freeport, TX 77541 (US).		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  Published With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: ALPHA-OLEFIN/VINYL OR VINYLIDENE AROMATIC INTERPOLYMER PRODUCT AND PROCESS FOR MAKING SAME USING MULTIPLE CATALYST SYSTEMS



## (57) Abstract

The present invention relates to a thermoplastic interpolymer product comprising an  $\alpha$ -olefin interpolymerized with at least one vinyl or vinylidene aromatic monomer and/or at least one hindered aliphatic or cycloaliphatic vinyl or vinylidene aromatic monomer and, in at least one aspect, is characterized as having substantially synergistic thermal properties. The invention also relates to a process for manufacturing the interpolymer product wherein the process employs two or more single site or metallocene catalyst systems in at least one reaction environment and wherein at least two of the catalyst systems have (a) different monomer incorporation capabilities or reactivities and (b) the same or, optionally, different monomer sequencing and/or tacticity characteristics. With unique thermal property attributes, the interpolymer product is useful, for example, for impact, bitumen and asphalt modification, adhesives, dispersions or latexes and fabricated articles such as, but not limited to, foams, films, sheet, moldings, thermoforms, profiles and fibers.

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ALPHA-OLEFIN/VINYL OR VINYLIDENE AROMATIC INTERPOLYMER  
PRODUCT AND PROCESS FOR MAKING SAME USING MULTIPLE  
CATALYST SYSTEMS

5

The present invention relates to a thermoplastic  
interpolymer product comprising an  $\alpha$ -olefin  
interpolymerized with at least one vinyl or vinylidene  
aromatic monomer and/or at least one hindered aliphatic or  
10 cycloaliphatic vinyl or vinylidene aromatic monomer and,  
in at least one aspect, is characterized as having  
substantially synergistic thermal properties. The  
invention also relates to a process for manufacturing the  
interpolymer product wherein the process comprises  
15 employing two or more single site catalyst systems in at  
least one reaction environment (or reactor) and wherein at  
least two of the catalyst systems have (a) different  
monomer incorporation capabilities or reactivities and (b)  
the same or, optionally, different monomer sequencing  
20 and/or tacticity characteristics. With unique thermal  
property attributes, the interpolymer product is useful,  
for example, for impact, bitumen and asphalt modification,  
adhesives, dispersions or latexes and fabricated articles  
such as, but not limited to, foams, films, sheet,  
25 moldings, thermoforms, profiles and fibers.

The generic class of materials covered by  $\alpha$ -  
olefin/vinyl or vinylidene aromatic and/or hindered  
aliphatic or cycloaliphatic vinyl or vinylidene  
interpolymers and including materials such as  
30 substantially random  $\alpha$ -olefin/vinyl aromatic interpolymers  
are known in the art and offer a range of material

structures and properties which makes them useful in various applications. For example, US Patent No. 5,460,818, describes substantially random  $\alpha$ -olefin/vinyl aromatic monomer interpolymers as compatibilizers for blends of polyethylene and polystyrene. However, known methods and procedures for manufacturing  $\alpha$ -olefin/vinyl or vinylidene aromatic and/or hindered aliphatic or cycloaliphatic vinyl or vinylidene interpolymers do not provide independent control of material properties and attributes. That is, crystallinity, melting point and glass transition characteristics are known to inevitably vary with comonomer concentration where increase concentrations result in lower crystallinities, melting point temperatures, glass transition temperatures and service temperatures.

There are several known methods for preparing  $\alpha$ -olefin/vinyl or vinylidene aromatic and/or hindered aliphatic or cycloaliphatic vinyl or vinylidene interpolymers such as those described by Francis J. Timmers et al. in U. S. Application No. 08/708,809, filed September 4, 1996; John G. Bradfute et al. (W. R. Grace & Co.) in WO 95/32095; R. B. Pannell (Exxon Chemical Patents, inc.) in WO 94/00500; and in Plastics Technology, p. 25 (September 1992).

Numerous other preparative methods for  $\alpha$ -olefin/vinyl or vinylidene aromatic and/or hindered aliphatic or cycloaliphatic vinyl or vinylidene interpolymers have been described in the literature. For example, Longo and Grassi (Makromol. Chem., Volume 191, pages 2387 to 2396 [1990]) and D'Anniello et al. (Journal of Applied Polymer

Science, Volume 58, pages 1701-1706 [1995]), reported the use of a catalytic system based on methylalumoxane (MAO) and cyclopentadienyltitanium trichloride ( $\text{CpTiCl}_3$ ) to prepare an ethylene-styrene copolymer. Xu and Lin

5 (Polymer Preprints, Am. Chem. Soc., Div. Polym. Chem., Volume 35, pages 686,687 [1994]), have reported copolymerization using a  $\text{MgCl}_2/\text{TiCl}_4/\text{NdCl}_3/\text{Al}(\text{iBu})_3$  catalyst to give random copolymers of styrene and propylene. Lu et al. (Journal of Applied Polymer Science, Volume 53, pages

10 1453 to 1460 [1994]), have described the copolymerization of ethylene and styrene using a  $\text{TiCl}_4/\text{NdCl}_3/\text{MgCl}_2/\text{Al}(\text{Et})_3$  catalyst. Sernetz and Mulhaupt, (Macromol. Chem. Phys., V. 197, pp. 1071-1083, 1997), have described the influence of polymerization conditions on the copolymerization of

15 styrene with ethylene using  $\text{Me}_2\text{Si}(\text{Me},\text{Cp})(\text{n-tert-butyl})\text{TiCl}_2/\text{Methylaluminoxane}$  Ziegler-Natta catalysts. Copolymers of ethylene and styrene produced by bridged metallocene catalysts have been described by Arai, Toshiaki and Suzuki (Polymer Preprints, Am. Chem. Soc.,

20 Div. Polym. Chem., Volume 38, pages 349, 350 [1997]). Also, random copolymers of ethylene and styrene having high isotacticity are disclosed in Polymer Preprints, Vol. 39, no. 1, March 1998 by Toru Aria et al.

Also several patent describe the manufacture of  $\alpha$ -

25 olefin/vinyl aromatic monomer interpolymers such as propylene/styrene and butene/styrene in U.S. Patent No. 5,244,996, issued to Mitsui Petrochemical Industries Ltd.; U.S. Patent No. 5,652,315, also issued to Mitsui Petrochemical Industries Ltd.; or DE 197 11 339 A1 to

30 Denki Kagaku Kogyo KK. Ethylene/styrene copolymer

produced by bridged metallocene catalysts are also described in U.S. Patent No. 5,652,315, issued to Mitsui Toatsu Chemicals, Inc.

Pseudo-random ethylene/vinyl aromatic interpolymers and the catalyst systems for making the same are disclosed in US Patent No. 5,703,187 and EP 416 815 A2.

US patent application number 08/991,836, filed December 16, 1997 and WO 98/10018 indicate that a suitable method for manufacturing substantially random ethylene/vinyl aromatic interpolymers involves polymerizing a mixture of polymerizable monomers in the presence of one or more metallocene or constrained geometry catalysts in combination with various cocatalysts. However, the exemplified compositions therein all involve the same single catalyst composition of a titanium-based constrained geometry catalyst together with tris (pentafluorophenyl)boron as the activator and methylaluminoxane as the cocatalyst. That is, all reported examples were monocatalyzed interpolymers. Furthermore, there is no explicit disclosure in these descriptions that interpolymers made using multiple catalyst systems can provide improved thermal properties such as substantially higher melting points at substantially comparable crystallinities or diffused  $T_g$  responses.

Blends comprising  $\alpha$ -olefin/vinylidene aromatic monomer and/or hindered aliphatic or cycloaliphatic vinylidene monomer interpolymers are described in WO 95/27755, in the names of Chung P. Park et al. and WO 98/10018, in the names of Martin J. Guest et al. All of

the exemplified compositions consisted of physical melt blend preparations using component interpolymers made from a single catalyst composition. That is, the blends were not made using an *in-situ* or multiple reactor  
5 interpolpolymerization technique, nor were they manufactured using multiple catalyst compositions and, as such, all component polymers were monocatalyzed.

Moreover, melt blending is not known to provide independent or unique control of thermal resistance,  
10 melting behavior and glass transition characteristics as no complete data of such attributes are reported in WO 95/27755 nor WO 98/10018. Thus it remains, although known  $\alpha$ -olefin/vinyl or vinylidene aromatic interpolymers have several important attributes, they also exhibit several  
15 important deficiencies. For example, known  $\alpha$ -olefin/vinyl or vinylidene aromatic interpolpolymer compositions, whether monocatalyzed or the melt blends, are characterized as having relatively low maximum service temperatures and narrow glass transition temperature ranges or widths (that  
20 is less than 15°C) which limit their usefulness for elevated temperature service/applications as well as for applications which require the effective glass transition to span across a broad temperatures range. It is an object of the present invention to solve the problem of  
25 deficient thermal characteristics exhibited by known  $\alpha$ -olefin/vinyl or vinylidene aromatic interpolymers.

We have discovered a new family of  $\alpha$ -olefin/vinyl aromatic interpolpolymer products which are characterized as having substantially synergistic and improved thermal  
30 characteristics. The broad aspect of the invention is an

interpolymer product comprising an  $\alpha$ -olefin  
interpolymerized with at least one vinyl or vinylidene  
aromatic monomer wherein the interpolymer product is  
characterized as having:

- 5           A1) a melting point, as determined using  
differential scanning calorimetry, equal to or greater  
than the product of the equation:

melting point =  $128 - 1.3333 \times \text{total weight percent}$   
interpolymerized vinyl and/or vinylidene aromatic monomer,

- 10           preferably, equal to or greater than the product of  
the equation:

melting point =  $144 - 1.53 \times \text{total weight percent}$   
interpolymerized vinyl and/or vinylidene aromatic monomer,

- 15           more preferably, equal to or greater than the  
product of the equation:

melting point =  $160 - 1.66667 \times \text{total weight percent}$   
interpolymerized vinyl and/or vinylidene aromatic monomer,  
or

- 20           A2) a highest peak melting point temperature (as  
determined using differential scanning calorimetry (DSC))  
or a maximum service temperature (as determined using  
thermal mechanical analysis (TMA)) equal to or greater  
than 16 percent, preferably 30 percent, more preferably 50  
percent higher than the melting point or maximum service  
25           temperature of a CAT2 monocatalyzed substantially random  
 $\alpha$ -olefin/vinyl or vinylidene aromatic monomer interpolymer  
having an equivalent total mol percent interpolymerized  
vinyl and/or vinylidene aromatic monomer concentration,

or



B) a glass transition temperature range or width at half peak temperature height of greater than or equal to 15°C, preferably greater than or equal to 20°C, more preferably greater than or equal to 25°C, most preferably greater than or equal to 30°C, as determined using dynamic mechanical spectroscopy (DMS) loss modulus ( $G''$ ) data.

In a preferred embodiment, the inventive interpolymer product comprises ethylene as the  $\alpha$ -olefin and styrene as the at least one vinyl or vinylidene aromatic monomer and is characterized as having:

A) a highest peak melting point temperature (as determined using differential scanning calorimetry (DSC)) or a maximum service temperature (as determined using thermal mechanical analysis (TMA)) equal to or greater than 16 percent, preferably 30 percent, more preferably 50 percent higher than the melting point or maximum service temperature of a CAT2 monocatalyzed substantially random ethylene/styrene interpolymer having an equivalent total mol percent interpolymerized vinyl and/or vinylidene concentration,

or

B) a glass transition temperature range or width at half peak temperature height of greater than or equal to 15°C, preferably greater than or equal to 20°C, more preferably greater than or equal to 25°C, most preferably greater than or equal to 30°C, as determined using dynamic mechanical spectroscopy (DMS) loss modulus ( $G''$ ) data.

In other embodiments, the interpolymer product is dominantly substantially random, random, or alternating (that is more than 50 weight percent of the product is

characterized as having the particular sequence).

Preferably, the product is more than 70 weight percent, more preferably more than 80 weight percent and most preferably more than 90 weight percent substantially

5 random. In especially preferred embodiments, the interpolymer product is substantially random with respect to all incorporated vinyl or vinylidene aromatic monomer sequences of more than three units.

In other embodiments, the interpolymer product can be  
10 partially substantially random, random, alternately, diadic, triadic, tetradic or any combination thereof. That is, the interpolymer product can be variably incorporated and optionally variably sequenced. For example, the interpolymer product can be variably  
15 incorporated and dominantly substantially random where the two catalyst systems (for example CAT1 and CAT2) employed both characteristically provide a substantially random monomer sequencing. Such is believed to be the case as to incorporation even where the incorporation ratio between  
20 the two catalyst systems is 50/50. The interpolymer product can be variably incorporated and variably sequenced where, for example, the two catalyst systems employed both characteristically provide a different monomer sequence.

25 In still other embodiments, the inventive interpolymer product can be variably incorporated and optionally variably sequenced and/or variably atactic, isotactic, syndiotactic or a combination thereof. That is, the inventive interpolymer product can have a mixed,  
30 the same or a different tacticity (that is atactic,

isotactic, syndiotactic or combinations thereof) with respect to any partial or total sequence variety. Of particular interest (especially for elastic article applications) is an embodiment where the interpolymer product has improved thermal property attributes and comprises random, substantially random or alternating (or any combination thereof) hard and soft segments or blocks.

Where the interpolymer has a high degree of alternating monomer sequencing (that is the interpolymer gives peaks at all three chemical shift regions of the main chain methylene and methyne carbons and the peak areas of these regions is not less than 70 percent of the total peak area of the main chain methylene and methyne carbons), a high degree of isotacticity (that is the isotactic diad is not less than 0.55) is most preferred

Another aspect of the invention is an interpolymer product comprising  $\alpha$ -olefin and at least one vinyl or vinylidene aromatic monomer made using at least two single site catalyst systems in at least one reaction environment or reactor wherein the catalyst systems are selected and operated to provide different monomer incorporation capabilities or reactivities.

A third aspect of the invention is a process for making an interpolymer product, the product comprising an  $\alpha$ -olefin interpolymerized with at least one vinyl or vinylidene aromatic monomer, the process comprising

- a) selecting at least two single site catalyst systems,
- b) feeding the catalysts systems to at least one reaction environment or reactor, and

c) controlling the reaction environment (or reactor), catalyst systems and interpolymerization conditions such that the catalyst systems operate or function at different vinyl or vinylidene aromatic monomer incorporation capabilities or interpolymerization reactivity rates.

In certain aspects, the inventive interpolymer product has surprisingly improved thermal properties. For example, thermal property attributes can be controlled independent of monomer concentration and substantially independent of crystallinity or glass transition peak temperature. In particular aspects, as unique features, the melting point and/or thermal resistance of the inventive interpolymer product is substantially higher than that of a comparative substantially random interpolymer having an equivalent vinyl or vinylidene aromatic concentration and/or substantially comparably crystallinity. Alternatively, in other aspects and when amorphous, the inventive interpolymer product is surprisingly characterized by a more diffuse (that is broader)  $T_g$  temperature range or width at equivalent vinyl or vinylidene aromatic concentration.

In particular embodiments, the inventive interpolymer product is characterized by various physical property enhancements such as, but not limited to, improved processability in terms of shear thinning and melt strength improvement from molecular weight control; improved mechanical properties such as impact resistance and tensile elongation; improved control of stress relaxation and elastic recovery attributes; improved

control of surface characteristics for enhancement such as paintability; and combinations thereof.

The commercial benefit of the present invention is now  $\alpha$ -olefin/vinyl or vinylidene aromatic interpolymers with improved thermal characteristics are available. With improvements such as, for example, significantly higher maximum service temperatures, it is now possible to provide elastic articles (for example waist bands in undergarments) which retain their elastic properties after exposure to elevated temperatures such as laundry dryers.

FIG. 1 shows the baseline method applied to the  $G''$  versus temperature curve of Inventive Example 13.

FIG. 2 is a plot of the highest peak melting point versus weight percent interpolymerized styrene for Inventive Examples 1 and 2 and comparative runs 3-12.

FIG. 3 is a plot of the maximum service temperature versus weight percent interpolymerized styrene for Inventive Examples 1 and 2 and comparative runs 3-5.

FIG. 4 is a plot of the weight percent crystallinity versus weight percent interpolymerized styrene for Inventive Examples 1 and 2 and comparative runs 3-12.

FIG. 5 is a plot of the  $T_g$  (by  $\tan \delta$ ) versus weight percent interpolymerized styrene for Inventive Example 13 and several monocatalyzed comparative runs.

FIG. 6 shows an overlay of the  $G''$  versus temperature curves for Inventive Example 13 and comparative run 14.

FIG. 7 shows an overlay of the  $G''$  versus temperature curves for comparative runs 15-17.

The term "interpolymer" is used herein to indicate a polymer wherein at least two different monomers are

polymerized. That is, the polymer contains a plurality of polymerized monomers as such two, three, four and so on.

The term "copolymer" as employed herein means a polymer wherein at least two different monomers are  
5 polymerized to form the copolymer. Thus, as used herein, there is overlap between the terms "interpolymer" and "copolymer" as, herein, both terms can refer to a polymer comprised of, for example, three polymerized monomers.

The term "different catalyst systems" is used herein  
10 in reference to catalyst systems that incorporate monomers at different amount during interpolymerization. While the term principally refers to catalyst systems having different chemical compositions relative to one another, the term generally refers to any difference that results  
15 in different monomer incorporation or different polymerization reactivities or rates. As such, the term also refers to differences in concentrations, operating conditions, injection methods or timing where the catalyst systems have the same chemical composition.

20 The term "variably incorporated" as used herein refers an interpolymer product manufactured using at least two catalyst systems wherein during interpolymerization the catalyst systems are operated at different incorporation or reactivity rates. For example, the  
25 interpolymer product having a total styrene content of 36 weight percent is variably incorporated where one catalyst system incorporates 22 weight percent styrene and the other catalyst system incorporates 48 weight percent styrene and the production split between the two catalyst  
30 systems is 47/53 weight percentages.

Suitable "alternating" interpolymers are those in which the aliphatic alpha-olefin monomer (A) and hindered vinylidene monomer (B) occur in repeat alternate sequences on the polymer chain in atactic or stereospecific  
5 structures (such as isotactic or syndiotactic) or in combinations of the general formula  $(AB)_n$ .

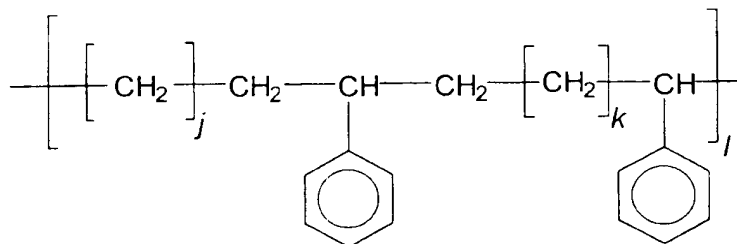
Suitable "random" interpolymers are those in which the monomer units are incorporated into the chain wherein there can exist various combinations of ordering including  
10 blockiness where either the aliphatic alpha-olefin monomer (A) or hindered vinylidene monomer (B) or both can be repeated adjacent to one another.

Substantially random ethylene/vinyl or vinylidene aromatic interpolymers are especially preferred  
15 interpolymer products of the present invention. Representative of substantially random ethylene/vinyl aromatic interpolymers are substantially random ethylene/styrene interpolymers.

The term "substantially random" in the substantially  
20 random interpolymer resulting from polymerizing one or more  $\alpha$ -olefin monomers and one or more vinyl or vinylidene aromatic monomers or hindered aliphatic or cycloaliphatic vinyl or vinylidene monomers, and optionally, with other polymerizable ethylenically unsaturated monomer(s) as used  
25 herein means that the distribution of the monomers of said interpolymer can be described by the Bernoulli statistical model or by a first or second order Markovian statistical model, as described by J. C. Randall in POLYMER SEQUENCE DETERMINATION, Carbon-13 NMR Method, Academic Press New  
30 York, 1977, pp. 71-78. Preferably, the substantially

random interpolymer resulting from polymerizing one or more  $\alpha$ -olefin monomers and one or more vinyl or vinylidene aromatic monomer, and optionally, with other polymerizable ethylenically unsaturated monomer(s) does not contain more than 15 percent of the total amount of vinyl or vinylidene aromatic monomer residue in blocks of vinyl or vinylidene aromatic monomer of more than 3 units. More preferably, the interpolymer is not characterized by a high degree of either isotacticity or syndiotacticity. This means that in the carbon-<sup>13</sup> NMR spectrum of the substantially random interpolymer the peak areas corresponding to the main chain methylene and methine carbons representing either meso diad sequences or racemic diad sequences should not exceed 75 percent of the total peak area of the main chain methylene and methine carbons.

Pseudorandom interpolymers are a subset of substantially random interpolymers. Pseudorandom interpolymers are characterized by an architecture in which all phenyl (or substituted phenyl) groups which are pendant from the polymer backbone are separated by two or more carbon backbone units. In other words, the pseudorandom interpolymers of the invention, in their noncrosslinked state, can be described by the following general formula (using styrene as the vinyl aromatic monomer and ethylene as the  $\alpha$ -olefin for illustration):





Noncrosslinked pseudorandom interpolymers are described in European Patent Publication 416,815-A.

While not wishing to be bound by any particular theory, it is believed that during the addition  
5 polymerization reaction of, for example, ethylene and styrene, in the presence of a constrained geometry catalyst as described below, if a styrene monomer is inserted into the growing polymer chain, the next monomer inserted will be an ethylene monomer or a styrene monomer  
10 inserted in an inverted or "tail-to-tail" fashion. It is believed that after an inverted or "tail-to-tail" styrene monomer is inserted, the next monomer will be ethylene, as the insertion of a second styrene monomer at this point would place it too close to the inverted styrene monomer,  
15 that is, less than two carbon backbone units away.

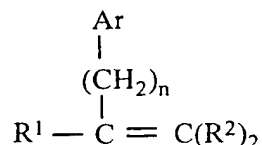
Preferably, the substantially random interpolpolymer will be characterized as largely atactic, as indicated by a  $^{13}\text{C}$ -NMR spectrum in which the peak areas corresponding to the main chain methylene and methine carbons  
20 representing either meso diad sequences or racemic diad sequences does not exceed 75 percent of the total peak area of the main chain methylene and methine carbons.

Substantially random interpolymers which are suitable for use in the present invention include, substantially  
25 random interpolymers prepared by polymerizing i) one or more  $\alpha$ -olefin monomers and ii) one or more vinyl or vinylidene aromatic monomers and/or one or more sterically hindered aliphatic or cycloaliphatic vinyl or vinylidene monomers, and optionally iii) other polymerizable  
30 ethylenically unsaturated monomer(s)

Suitable  $\alpha$ -olefins include for example,  $\alpha$ -olefins containing from 2 to 20, preferably from 2 to 12, more preferably from 2 to 8 carbon atoms. Particularly suitable are ethylene, propylene, butene-1, 4-methyl-1-pentene, hexene-1 or octene-1 or ethylene in combination with one or more of propylene, butene-1, 4-methyl-1-pentene, hexene-1 or octene-1. These  $\alpha$ -olefins do not contain an aromatic moiety.

Other optional polymerizable ethylenically unsaturated monomer(s) include norbornene and  $C_1$ - $C_{10}$  alkyl or  $C_6$ - $C_{10}$  aryl substituted norbornenes, with an exemplary interpolymer being ethylene/styrene/norbornene.

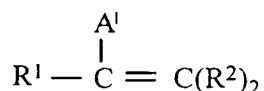
Suitable vinyl or vinylidene aromatic monomers which can be employed to prepare the interpolymer product include, for example, those represented by the following formula:



wherein  $\text{R}^1$  is selected from the group of radicals consisting of hydrogen and alkyl radicals containing from 1 to 4 carbon atoms, preferably hydrogen or methyl; each  $\text{R}^2$  is independently selected from the group of radicals consisting of hydrogen and alkyl radicals containing from 1 to 4 carbon atoms, preferably hydrogen or methyl; Ar is a phenyl group or a phenyl group substituted with from 1 to 5 substituents selected from the group consisting of halo,  $C_1$ - $C_4$ -alkyl, and  $C_1$ - $C_4$ -haloalkyl; and n has a value from zero to about 4, preferably from zero to about 2,

most preferably zero. Particularly suitable such monomers include styrene and lower alkyl- or halogen-substituted derivatives thereof. Exemplary monovinyl or monovinylidene aromatic monomers include styrene, vinyl  
5 toluene,  $\alpha$ -methylstyrene, t-butyl styrene or chlorostyrene, including all isomers of these compounds. Preferred monomers include styrene,  $\alpha$ -methyl styrene, the lower alkyl-(C<sub>1</sub>-C<sub>4</sub>) or phenyl-ring substituted derivatives of styrene, such as for example, ortho-, meta-, and para-  
10 methylstyrene, the ring halogenated styrenes, para-vinyl toluene or mixtures thereof. A more preferred aromatic monovinyl monomer is styrene.

By the term "sterically hindered aliphatic or cycloaliphatic vinyl or vinylidene monomers", it is meant  
15 addition polymerizable vinyl or vinylidene monomers corresponding to the formula:



wherein A<sup>1</sup> is a sterically bulky, aliphatic or cycloaliphatic substituent of up to 20 carbons, R<sup>1</sup> is  
20 selected from the group of radicals consisting of hydrogen and alkyl radicals containing from 1 to 4 carbon atoms, preferably hydrogen or methyl; each R<sup>2</sup> is independently selected from the group of radicals consisting of hydrogen and alkyl radicals containing from 1 to 4 carbon atoms,  
25 preferably hydrogen or methyl; or alternatively R<sup>1</sup> and A<sup>1</sup> together form a ring system.

By the term "sterically bulky" is meant that the monomer bearing this substituent is normally incapable of

addition polymerization by standard Ziegler-Natta polymerization catalysts at a rate comparable with ethylene polymerizations.

5  $\alpha$ -Olefin monomers containing from 2 to 20 carbon atoms and having a linear aliphatic structure such as ethylene, propylene, butene-1, hexene-1, heptene-1 and octene-1 are not considered to be sterically hindered aliphatic monomers.

Preferred sterically hindered aliphatic or  
10 cycloaliphatic vinyl or vinylidene compounds are monomers in which one of the carbon atoms bearing ethylenic unsaturation is tertiary or quaternary substituted. Examples of such substituents include cyclic aliphatic groups such as cyclohexyl, cyclohexenyl, cyclooctenyl, or  
15 ring alkyl or aryl substituted derivatives thereof, tert-butyl or norbornyl. Most preferred sterically hindered aliphatic or cycloaliphatic vinyl or vinylidene compounds are the various isomeric vinyl-ring substituted derivatives of cyclohexene and substituted cyclohexenes,  
20 and 5-ethylidene-2-norbornene. Especially suitable are 1-, 3-, and 4-vinylcyclohexene.

The inventive interpolymer product usually contains from 5 to 65, preferably from 5 to 55, more preferably from 10 to 50 mole percent of at least one vinyl or  
25 vinylidene aromatic monomer; or sterically hindered aliphatic or cycloaliphatic vinyl or vinylidene monomer; or both; and from 35 to 95, preferably from 45 to 95, more preferably from 50 to 90 mole percent of at least one aliphatic  $\alpha$ -olefin having from 2 to 20 carbon atoms.

Other optional polymerizable ethylenically unsaturated monomer(s) include strained ring olefins such as norbornene and C<sub>1</sub>-C<sub>10</sub>-alkyl or C<sub>6</sub>-C<sub>10</sub>-aryl substituted norbornenes, with an exemplary substantially random  
5 interpolymer being ethylene/styrene/norbornene.

The most preferred inventive interpolymer product are interpolymers of ethylene and styrene and interpolymers of ethylene, styrene and at least one  $\alpha$ -olefin containing from 3 to 8 carbon atoms.

10 The number average molecular weight ( $M_n$ ) of the inventive interpolymer product is usually greater than 5,000, preferably from 20,000 to 1,000,000, more preferably from 50,000 to 500,000.

Semi-crystalline inventive interpolymer products  
15 (that is those having a measurably crystallinity using differential scanning calorimetry) can be conveniently characterized by DSC crystallinity, DMS glass transition temperature, DSC highest peak melting point temperature and maximum service temperature by thermal mechanical  
20 analysis (TMA). Conversely, amorphous inventive interpolymer products (that is those having no measurable crystallinity using differential scanning calorimetry and which typically contain greater than 48 weight percent vinyl or vinylidene aromatic monomer) are conveniently  
25 characterized by glass transition characteristics (that is,  $T_g$  and peak widths at half peak temperature height) as determined using dynamic mechanical spectroscopy (DMS).

The glass transition temperature ( $T_g$ ) of the inventive interpolymer product is preferably in the range from -40°C  
30 to +60°C, more preferably from -30°C to +50°C, most

preferably from -10°C to +40°C, as measured by differential mechanical scanning (DMS) using loss modulus (G'') data. The melting point of the inventive semicrystalline interpolymer product is preferably in the range from 0°C to 5 160°C, as determined using differential scanning calorimetry (DSC).

In especially preferred embodiments, the inventive interpolymer product has a polydispersity greater than 4, preferably greater than 7, as determined using gel 10 permeation chromatography (GPC).

The inventive interpolymer product may be modified by typical grafting, hydrogenation, functionalizing, or other reactions well known to those skilled in the art. The interpolymer product may be readily sulfonated or 15 chlorinated to provide functionalized derivatives according to established techniques. The interpolymer product may also be modified by various chain extending or crosslinking processes including, but not limited to peroxide-, silane-, sulfur-, radiation-, or azide-based 20 cure systems. A full description of the various cross-linking technologies is described in copending US Patent Application Nos. 08/921,641 and 08/921,642, both filed on August 27, 1997.

Dual cure systems, which use a combination of heat, 25 moisture cure, and/or radiation steps, may also be effectively employed. Dual cure systems are disclosed and claimed in US Patent Application Serial No. 536,022, filed on September 29, 1995, in the names of K. L. Walton and S. V. Karande. Particularly desirable dual-cure systems 30 employ peroxide crosslinking agents in conjunction with

silane crosslinking agents, peroxide crosslinking agents in conjunction with radiation, sulfur-containing crosslinking agents in conjunction with silane crosslinking agents, and combinations thereof.

5       The inventive interpolymer product may also be modified by various other crosslinking processes including, but not limited to, the incorporation of a diene component as a termonomer in its preparation and subsequent crosslinking by the aforementioned methods and  
10 further methods including vulcanization via the vinyl group using sulfur for example as the crosslinking agent.

      The interpolymer product can also be mixed or blended (including melt blended) with other natural and/or synthetic materials such as, including, but not limited  
15 to, conventional (that is those not variably incorporated)  $\alpha$ -olefin/vinyl or vinylidene aromatic interpolymers, substantially linear ethylene interpolymers, homogeneously branched linear ethylene interpolymers, heterogeneously branched linear ethylene interpolymers (for example,  
20 linear low density polyethylene (LLDPE), medium density polyethylene (MDPE), high density polyethylene (HDPE) and ultra low or very low density polyethylene (ULDPE or VLDPE)), elastomers, rubbers, polystyrene (especially high impact polystyrenes (HIPS)), styrene block polymers (for  
25 example styrene butadiene block copolymers, styrene/ethylene propylene/styrene block copolymers, styrene/ethylene-butylene/styrene block copolymers, styrene/isoprene/styrene block copolymers, and styrene/butadiene/styrene block copolymers), polyethers  
30 (especially aromatic polyethers), polypropylene,

polysulfones, polycarbonates, polyamides, ABS, epoxies, ethylene/propylene interpolymers, anhydride modified polyethylenes (for example, maleic anhydride grafted LLDPE and HDPE) as well as high pressure polyethylenes such as, 5 for example, but not limited to, low density polyethylene (LDPE), ethylene/acrylic acid (EAA) interpolymers and ionomers, ethylene/methacrylic acid (EMAA) interpolymers and ionomers, ethylene/vinyl acetate (EVA) interpolymers and ethylene/methacrylate (EMA) interpolymers, and any 10 combination thereof.

The inventive interpolymer product is manufacture using (that is, by contacting monomers with) at least two single site or metallocene catalyst systems in at least one reaction environment or reactor. In particular 15 embodiments, the process comprises at two reaction environments or reactors operated in series or parallel, and preferably in series configuration.

The interpolymerization process can be solution, gas phase, particle form (that is slurry or dispersion 20 polymerization) type or any combination thereof such as where multiple reaction environments or reactors are employed and at least one environment or reactor is in solution mode and at least one other is in particle form or gas phase mode. However, a solution 25 interpolymerization process is preferred.

Preferably, interpolymerization operating conditions comprise pressures from about atmospheric up to about 3,000 atmospheres and temperatures from -30°C to 200°C.

The at least one reaction environment or reactor may 30 be a sphere, stirred tank, tube or loop configuration or

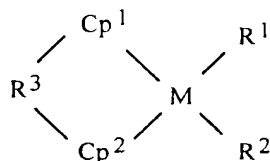


design or any combination thereof such as where multiple reaction environments or reactors are employed. However, a loop configuration (including a multiple loop configuration) is preferred due to its tendency to provide improved product conversion and productivity.

One method of preparation of the substantially random interpolymers includes polymerizing a mixture of polymerizable monomers in the presence of one or more metallocene or constrained geometry catalysts in combination with various cocatalysts, as described in EP-A-0,416,815 by James C. Stevens et al. and US Patent No. 5,703,187 by Francis J. Timmers. Such a method of preparation of the substantially random interpolymers includes polymerizing a mixture of polymerizable monomers in the presence of one or more metallocene or constrained geometry catalysts in combination with various cocatalysts. Preferred operating conditions for such polymerization reactions are pressures from atmospheric up to 3000 atmospheres and temperatures from -30°C to 200°C. Polymerizations and unreacted monomer removal at temperatures above the autopolymerization temperature of the respective monomers may result in formation of some amounts of homopolymer polymerization products resulting from free radical polymerization.

Examples of suitable catalysts and methods for preparing the substantially random interpolymers are disclosed in U.S. Application Serial No. 702,475, filed May 20, 1991 (EP-A-514,828); as well as U.S. Patents: 5,055,438; 5,057,475; 5,096,867; 5,064,802; 5,132,380; 5,189,192; 5,321,106; 5,347,024; 5,350,723; 5,374,696; 5,399,635; 5,470,993; 5,703,187; and 5,721,185.

The substantially random  $\alpha$ -olefin/vinyl aromatic interpolymers can also be prepared by the methods described in JP 07/278230 employing compounds shown by the general formula



5 where  $\text{Cp}^1$  and  $\text{Cp}^2$  are cyclopentadienyl groups, indenyl groups, fluorenyl groups, or substituents of these, independently of each other;  $\text{R}^1$  and  $\text{R}^2$  are hydrogen atoms, halogen atoms, hydrocarbon groups with carbon numbers of 1-12, alkoxy groups, or aryloxy groups, independently of each other; M is a group IV metal, preferably Zr or Hf, most preferably Zr; and  $\text{R}^3$  is an alkylene group or silanediyl group used to cross-link  $\text{Cp}^1$  and  $\text{Cp}^2$ .

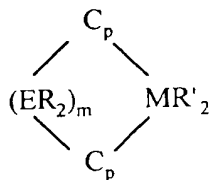
15 The substantially random  $\alpha$ -olefin/vinyl aromatic interpolymers can also be prepared by the methods described by John G. Bradfute et al. (W. R. Grace & Co.) in WO 95/32095; by R. B. Pannell (Exxon Chemical Patents, Inc.) in WO 94/00500; and in Plastics Technology, p. 25 (September 1992).

20 Also suitable are the substantially random interpolymers which comprise at least one  $\alpha$ -olefin/vinyl aromatic/vinyl aromatic/ $\alpha$ -olefin tetrad disclosed in U. S. Application No. 08/708,809 filed September 4, 1996 and WO 98/09999 both by Francis J. Timmers et al. These  
25 interpolymers contain additional signals in their carbon-13 NMR spectra with intensities greater than three times the peak to peak noise. These signals appear in the chemical shift range 43.70 - 44.25 ppm and 38.0 - 38.5

ppm. Specifically, major peaks are observed at 44.1, 43.9, and 38.2 ppm. A proton test NMR experiment indicates that the signals in the chemical shift region 43.70 - 44.25 ppm are methine carbons and the signals in  
 5 the region 38.0 - 38.5 ppm are methylene carbons.

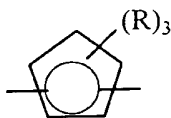
It is believed that these new signals are due to sequences involving two head-to-tail vinyl aromatic monomer insertions preceded and followed by at least one  $\alpha$ -olefin insertion, for example an  
 10 ethylene/styrene/styrene/ethylene tetrad wherein the styrene monomer insertions of said tetrads occur exclusively in a 1,2 (head to tail) manner. It is understood by one skilled in the art that for such tetrads involving a vinyl aromatic monomer other than styrene and  
 15 an  $\alpha$ -olefin other than ethylene that the ethylene/vinyl aromatic monomer/vinyl aromatic monomer/ethylene tetrad will give rise to similar carbon-13 NMR peaks but with slightly different chemical shifts.

Other suitable catalysts for use in the present  
 20 invention include, but are not limited to, those represented by the formula:



wherein each  $C_p$  is independently, each occurrence, a substituted cyclopentadienyl group  $\pi$ -bound to M; E is C or  
 25 Si; M is a group IV metal, preferably Zr or Hf, most preferably Zr; each R is independently, each occurrence, H, hydrocarbyl, silahydrocarbyl, or hydrocarbylsilyl,

containing up to about 30 preferably from 1 to 20 more preferably from 1 to 10 carbon or silicon atoms; each R' is independently, each occurrence, hydrogen, halo, hydrocarbyl, hydrocarbyloxy, silahydrocarbyl, hydrocarbylsilyl containing up to 30, preferably from 1 to 20, more preferably from 1 to 10 carbon or silicon atoms or two R' groups together can be a C<sub>1</sub>-C<sub>10</sub> hydrocarbyl substituted 1,3-butadiene; m is 1 or 2; and optionally, but preferably in the presence of an activating cocatalyst. Particularly, suitable substituted cyclopentadienyl groups include those illustrated by the formula:



wherein each R is independently, each occurrence, H, hydrocarbyl, silahydrocarbyl, or hydrocarbylsilyl, containing up to 30, preferably from 1 to 20, more preferably from 1 to 10 carbon or silicon atoms or two R groups together form a divalent derivative of such group. Preferably, R independently each occurrence is (including where appropriate all isomers) hydrogen, methyl, ethyl, propyl, butyl, pentyl, hexyl, benzyl, phenyl or silyl or (where appropriate) two such R groups are linked together forming a fused ring system such as indenyl, fluorenyl, tetrahydroindenyl, tetrahydrofluorenyl, or octahydrofluorenyl.

Particularly preferred catalysts include, for example, racemic-(dimethylsilanediyl(2-methyl-4-phenylindenyl))zirconium dichloride, racemic-(dimethylsilanediyl(2-methyl-4-phenylindenyl))zirconium

1,4-diphenyl-1,3-butadiene, racemic-(dimethylsilanediyl(2-methyl-4-phenylindenyl))zirconium di-C<sub>1-4</sub> alkyl, racemic-(dimethylsilanediyl(2-methyl-4-phenylindenyl))zirconium di-C<sub>1-4</sub> alkoxide, or any combination thereof .

5        Also included are the titanium-based catalysts, [N-(1,1-dimethylethyl)-1,1-dimethyl-1-[(1,2,3,4,5-h)-1,5,6,7-tetrahydro-s-indacen-1-yl]silanaminato(2-)-N]titanium dimethyl; (1-indenyl)(tert-butylamido)dimethyl-silane titanium dimethyl; ((3-tert-butyl)(1,2,3,4,5-h)-1-  
10 indenyl)(tert-butylamido) dimethylsilane titanium dimethyl; and ((3-iso-propyl)(1,2,3,4,5-h)-1-indenyl)(tert-butyl amido)dimethylsilane titanium dimethyl, or any combination thereof .

Other suitable catalyst systems for use as at least  
15 one, both or all of the least two catalyst systems required by the inventive process include, but are not limited to, those described by Longo and Grassi in Makromol. Chem., Volume 191, pages 2387 to 2396 [1990]; D'Anniello et al. in Journal of Applied Polymer Science,  
20 Volume 58, pages 1701-1706 [1995]; Xu and Lin in Polymer Preprints, Am.Chem.Soc., Div. Polym. Chem., Volume 35, pages 686,687 [1994]; Lu et al. in Journal of Applied Polymer Science, Volume 53, pages 1453 to 1460 [1994]; Sernetz and Mulhaupt, in Macromol. Chem. Phys., v. 197, pp 1071-1083,  
25 1997); and Arai, Toshiaki and Suzuki in Polymer Preprints, Am.Chem.Soc., Div. Polym. Chem., Volume 38, pages 349, 350 [1997] .

Still other suitable catalyst systems for use as at least one, both or all of the least two catalyst systems  
30 required by the inventive process include, but are not

limited to, those described or used in Plastics Technology,  
p. 25 (September 1992); WO 98,10018 by Martin J. Guest et  
al; WO 95/27755 by Chung P. Park et al.; WO 95/32095 by John  
G. Bradfute et al. (W. R. Grace & Co.); WO 94/00500 by R. B.  
5 Pannell (Exxon Chemical Patents, Inc.); WO 97/42240 by Van  
Tol et al.; U.S. Application No. 07/545,403, filed July 3,  
1990 corresponding to EP-A-416,815; U.S. Application No.  
07/702,475, filed May 20, 1991 corresponding to EP-A-  
514,828; U.S. Application No. 07/876,268, filed May 1, 1992  
10 corresponding to EP-A-520,732; U.S. Application No.  
08/241,523, filed May 12, 1994; U.S. Application No.  
08/991,836, filed December 16, 1997; as well as EP 0 892  
014; DE 197 11 339; DE 195 42 356 based on WO 97/18248; and  
U.S. Patent Nos: 5,460,818; 5,62,315; 5,703,187; 5,055,438;  
15 5,057,475; 5,096,867; 5,064,802; 5,132,380; 5,189,192;  
5,321,106; 5,347,024; 5,043,408; 5,350,723; 5,374,696;  
5,399,635; 5,460,993; 5,244,996; and 5,556,928.

Other particularly suitable catalyst systems include,  
but are not limited to, that described by Francis J.  
20 Timmers et al. in U. S. Application No. 08/708,809, filed  
September 4, 1996, and those based on the cation,  $\eta^1:\eta^5$ -  
tert-Butyl(dimethyl-fluorenylsilyl)-  
amido{bis(trimethylsilyl)methyl}titanium(II), described by  
Guangxue Xu, Institute of Polymer Science, Zhongshan  
25 University, Guangzhou 510275.

The preferred class of single site or metallocene  
catalyst system for use in the present invention as at  
least one, both or all of the at least two catalyst  
systems is a constrained geometry catalyst system. More  
30 preferably, both and most preferably all of the at least

two catalyst systems are constrained geometry catalyst systems.

The interpolymer product with its unique thermal property attributes is useful in a variety of applications including, for example, for impact, bitumen and asphalt modification, adhesives, dispersions or latexes and fabricated articles such as, but not limited to, foams, films, sheet, moldings (especially compression and injection molding), coatings (especially extrusion coating) thermoforms, profiles and fibers (especially elastic fibers and nonwoven fabrics or composites).

#### Test Methods

The molecular weight and molecular weight distribution of the interpolymer product of the present invention were determined using gel permeation chromatography (GPC) procedures and methods.

The melting point and weight percent crystallinity of the interpolymer product were conveniently determined by differential scanning calorimetry (DSC) using a Dupont DSC-910 unit. In order to eliminate any previous thermal history, samples were first heated to 200°C. Heating and cooling curves were recorded at 10°C/minute. Melting (from second heat) and crystallization temperatures were recorded from the peak temperatures of the endotherm and exotherm, respectively. The peak with the highest amplitude was taken as the melting point temperature for the sample. The highest amplitude requirement was especially important where a curve showed multiple peaks or a peak was associated with a shoulder or hump. Weight

percent crystallinity (based on the total weight of the interpolymer product) was taken from an integration of the area under the endothermic curve to provide heat of fusion (in Joules/gram) which was then divided by 292

5 Joules/gram.

The glass transition temperature of the interpolymer product was determined using solid state dynamic mechanical spectroscopy (DMS) wherein compression molded samples were tested using a Rheometrics 800E mechanical spectrometer. Compression molded sample preparation was performed by melting the sample at 190°C for 3 minutes and compression molding at 190°C and under 20,000 lbs. (9072 kg) of pressure for another 2 minutes. Subsequently, the molten material was quenched in a press equilibrated to room temperature. The DMS testing was performed in torsional rectangular geometry mode under a constant nitrogen purge of about 2 scm. Samples were cooled to -100°C and run at a fixed oscillation frequency of 10 rad/sec using a torsional set strain of 0.05 percent. Loss modulus ( $G''$ ) data from ramped temperatures were collected isothermally at 5°C intervals. From a plot of loss modulus ( $G''$ ) versus temperature in degrees Celsius, the peak with the highest amplitude (in dynes/cm<sup>2</sup>) was taken as the glass transition temperature (peak  $T_g$  temperature) in °C for the sample.

The plot of loss modulus ( $G''$ ) versus temperature in degrees Celsius was also used to determine the peak width at half the height of the peak  $T_g$  temperature for the inventive interpolymer product. The baseline of the loss modulus versus temperature plot was conveniently drawn



using the baseline method wherein a straight line tangent to the  $G''$  versus temperature curve was drawn as illustrated in FIG. 1. Half peak height (in dynes/cm<sup>2</sup>) was the value (in dynes/cm<sup>2</sup>) at the apex of the peak with  
5 highest amplitude divided by 2. The glass transition temperature range or width was the measure in °C across the peak at half height. For particular precision, the x-y coordinates at the apex of the peak with the highest amplitude and at that peak's half height can be determined  
10 using DMS software add-ons or by importing the curve into a data analysis software package such as, for example, ORIGIN supplied by MicroCal which features cursor displays or assignments for the coordinates.

The maximum service temperature of the inventive  
15 interpolymer product was conveniently determined using a thermal mechanical analyzer (Perkin-Elmer TMA 7 series). Samples were scanned at 5 °C/minute and the load is set at 1 Newton. The point at which the TMA probe penetrated 1 mm into the sample was taken as the maximum service temperature for the  
20 sample.

The weight percent styrene and atactic polystyrene for the interpolymer product was conveniently determined using proton nuclear magnetic resonance (<sup>1</sup>H N.M.R). In the determinations, NMR samples were prepared in 1, 1, 2, 2-  
25 tetrachloroethane-d<sub>2</sub> (TCE-d<sub>2</sub>) at 1.6 - 3.2 percent polymer by weight. For each determination, product was weighed directly into a 5 mm sample tube, a 0.75 mL aliquot of TCE-d<sub>2</sub> was added by syringe and the tube was capped with a tight-fitting polyethylene cap. The sample was heated in  
30 a water bath at 85°C to soften the sample. To provide

mixing, the capped samples were occasionally brought to reflux about three separate times for about 15 seconds using a heat gun. The sample was then loaded into the Proton NMR unit immediately after the last reflux  
5 subsided.

Proton NMR spectra were accumulated on a Varian VXR 300 with the sample probe at 80°C and referenced to the residual protons of TCE-d<sub>2</sub> at 5.99 ppm. Delay times were about 1 second and data were collected in triplicate on  
10 each sample. The total analysis time per sample was about 10 minutes and the instrumental conditions were as follows:

Varian VXR-300, standard <sup>1</sup>H:  
Sweep Width, 5000 Hz  
15 Acquisition Time, 3.002 sec  
Pulse Width, 8 μsec  
Frequency, 300 MHz  
Delay, 1 sec  
Transients, 16

20 Initially, a <sup>1</sup>H NMR spectrum for a sample of the polystyrene, STYRON™ 680 (available from the Dow Chemical Company, Midland, MI) was acquired with a delay time of one second. The protons were "labeled": β, branch; α, alpha; o, ortho; m, meta; p, para, as shown in Figure 1 of  
25 U.S. Patent Application No. 08/991,836.

Integrals were measured around the labeled protons. Integral A<sub>7.1</sub> (aromatic, around 7.1 ppm) is believed to be the three ortho/para protons; and integral A<sub>6.6</sub> (aromatic, around 6.6 ppm) the two meta protons. The two aliphatic  
30 protons labeled α resonated at 1.5 ppm; and the single

proton labeled  $\beta$  resonated at 1.9 ppm. The aliphatic region was integrated from about 0.8 to 2.5 ppm and was referred to as  $A_{a1}$ .

Region  $A_{6.6}$  was assigned the value of 1. Ratio A1 was the integral  $A_{a1} / A_{6.6}$ . All spectra collected had a 1.5: 1: 1.5 integration ratio of (o+p) : m : ( $\alpha$ +b). The ratio of aromatic to aliphatic protons was 5 to 3. The aliphatic ratio was 2 to 1.

The following equations were used to determine the degree of styrene incorporation in the interpolymers product:

$$(C \text{ Phenyl}) = C_{7.1} + A_{7.1} - (1.5 \times A_{6.6})$$

$$(C \text{ Aliphatic}) = C_{a1} - (1.5 \times A_{6.6})$$

$$s_c = (C \text{ Phenyl}) / 5$$

$$e_c = (C \text{ Aliphatic} - (3 \times s_c)) / 4$$

$$E = e_c / (e_c + s_c)$$

$$S_c = s_c / (e_c + s_c)$$

and the following equations were used to calculate the mol percent ethylene and styrene in the interpolymers products.

$$Wt\%E = \frac{E * 28}{(E * 28) + (S_c * 104)} (100)$$

and

$$Wt\%S = \frac{S_c * 104}{(E * 28) + (S_c * 104)} (100)$$

where  $s_c$  and  $e_c$  are styrene and ethylene proton fractions in the interpolymers product, respectively, and  $S_c$

and E are mole fractions of styrene monomer and ethylene monomer in the interpolymer product, respectively.

The weight percent of aPS in the interpolymer product was determined by the following equation:

$$\text{Wt\%aPS} = \frac{(\text{Wt\%S}) * \left( \frac{A_{6.6}/2}{S_c} \right)}{100 + \left[ (\text{Wt\%S}) * \left( \frac{A_{6.6}/2}{S_c} \right) \right]} * 100$$

5

The total styrene content can also be determined by quantitative Fourier Transform Infrared spectroscopy (FTIR) and by Raman spectroscopy.

#### 10 Examples 1, 2 and 13

Polymerization experiments were performed to manufacture Inventive Examples 1, 2 and 13 using a 1 gallon stirred Autoclave Engineers reactor. For each example, the reactor was charged with the desired amounts  
 15 of toluene and styrene using a mass flow meter. Hydrogen was added by expansion from a 75 mL vessel, then the reactor was heated to the desired polymerization temperature and saturated with ethylene to the desired pressure. The catalyst was prepared in a dry-box by  
 20 successively adding solutions of MMAO-3A (Akzo Nobel);  $B(C_6F_5)_3$  (Boulder Scientific); CAT1 (Titanium, [1,1'-(h4-1,3-butadiene-1,4-diyl)bis[benzene]] [1-[(1,2,3,3a,11b-h)-1H-cyclopenta[1]phenanthren-1-yl]-N-(1,1-dimethylethyl)-1,1-dimethylsilanaminato(2-)-kN] - (CAS# 199876-47-6)); and  
 25 CAT2 (that is Titanium, [N-(1,1-dimethylethyl)-1,1-dimethyl-1-[(1,2,3,4,5-h)-2,3,4,5-tetramethyl-2,4-

cyclopentadien-1-yl]silanaminato(2-)-kN] [(1,2,3,4-h)-1,3-pentadiene]- (CAS# 169104-71-6)) to enough additional solvent to give a total volume of 12 mL. The catalyst solution was then transferred by syringe to a catalyst addition loop and injected into the reactor over approximately 2 minutes using a flow of high pressure solvent (toluene). The polymerization was allowed to proceed for 10 minutes while feeding ethylene on demand to maintain the desired pressure. The amount of ethylene consumed during the reaction was monitored using a mass flow meter. The interpolymer product solution was dumped from the reactor into a nitrogen-purged glass kettle. An aliquot of an additive solution (66.7 g of IRGAFOS<sup>®</sup> 168 and 33.3 g of IRGANOX<sup>®</sup> 1010, both supplied by Ciba Specialty Chemicals, in 500 mL of toluene) was added to this kettle in the amounts noted in Table 1 and the solution stirred thoroughly. The interpolymer product solution was dumped into a tray, air dried for several days, then thoroughly dried in a vacuum oven. The weights of the interpolymer products were recorded and their efficiencies calculated as grams of polymer per gram of titanium.

Table 1

Inventive Example	1	2	13
Temperature, (°C)	90	95	75
C <sub>2</sub> Pressure, (psig)	200	300	100
C <sub>2</sub> loaded, (g)	85.0	119.7	48.5
Toluene, (g)	800	800	600
Styrene, (g)	800	800	1000
H <sub>2</sub> , (psig)	50	25	25
H <sub>2</sub> , (mmol)	10.4	5.2	5.2
CAT2 ( mol)			
CAT1 ( mol)			

Ti/B/Al*			
C <sub>2</sub> Max Rate, (g/min)	41.2	42.5	3.7
C <sub>2</sub> Total, (g)	117.1	111.7	21.5
Additive Solution (mL)	2.2	2.3	0.4
Polymer Yield, g poly	246.0	141.2	68.6
Efficiency (g poly/g Ti)	427,975	267,983	130,195
Mw	269.6	244.3	381.5
Mn	34.2	21.7	22.5
Mw/Mn	7.9	11.3	17.0
% Interpolymerized	47.8	35.8	64.8
Styrene by wt. (NMR)			
%aPS by wt. (NMR)	3.3	5.4	13.0

\*Refers to molar ratio of Ti(CAT1 + CAT2) to B(C<sub>6</sub>F<sub>5</sub>) and MMAO-3A

#### Comparative Runs 3-12, 14, 16 and 17

- The same polymerization run as described above for
- 5 Inventive Example 1 was separately repeated, except only CAT1 (with the same activator and cocatalyst and molar ratios) was used to manufacture comparative runs 3-7 and only CAT2 1 (with the same activator and cocatalyst and molar ratios) was used to manufacture comparative runs 8-12, 14, 16 and 17. That is,
- 10 these comparative runs were all monocatalyzed.

Comparative Run 15

Comparative run 15 was prepared from a melt blend of two component polymers (comparative runs 16 and 17). The actual melt blending was performed using a Haake mixer equipped with a Rheomix 3000 bowl. About 180 grams of the component polymers (total) were first dry blended, then fed into the mixer and permitted to equilibrate to 190°C. The feeding and temperature equilibration took about 3 to 5 min. The molten material was mixed at 190°C and 40 rpm for about 10 minutes and then removed from the mixer and permitted to cool to ambient.

The physical properties of the Inventive Examples 1 and 2 and comparative runs 3-12 were determined according to procedures and methods described herein above. The results of these determinations are reported in Table 2.

Table 2

Example	Wt% Styrene	DSC Melting Point, °C	DSC Wt% Crystallinity	TMA Max. Service Temp., °C
Inv. Ex 1	36	100	15	99
Inv. Ex 2	48	80	6	66
Run 3	42	26	3	50
Run 4	35	54	10	64
Run 5	30	61	13	74
Run 6	47.8	20	1	ND
Run 7	35.8	52	10	ND
Run 8	28	77	18	ND
Run 9	47.8	43	3	ND
Run 10	35.8	70	15	ND
Run 11	30.7	69	8	ND
Run 12	22	84	17	ND

ND denotes not determined.

The glass transition temperature and temperature range or width was determined for Inventive Example 13 and several other comparative runs, including the melt blended

sample (comparative run 15). Table 3 reports the glass transition test results.

Table 3

Example	Wt% Styrene	DMS T <sub>g</sub> Temp., °C	T <sub>g</sub> Temp Range or Width, °C
Inv. Ex 13	65	-11, 5*	34
Inv. Ex 13	65	15	
Run 14	66	14*	10
Run 14	66	20	
Run 15	65	2, 24*	11, 10
Run 16	73	25*	10
Run 16	73	31	
Run 17	58	-3*	11
Run 17	58	3	
Run 18	26	-7	
Run 19	52	-2	
Run 20	48	-5	
Run 21	56	3	
Run 22	67	21	

\*Denotes the glass transition temperature was determined from G" data as opposed to tan  $\delta$  (G"/G') data. All T<sub>g</sub> width determination were performed using G" data.

FIG. 2 and 3 show Inventive Examples 1 and 2 exhibit substantially synergistic thermal properties. The DSC melting point and TMA maximum service temperature of these semi-crystalline interpolymer products were significantly improved over monocatalyzed interpolymers.

In contrast to FIG. 2 and 3, FIG. 4 indicates that the weight percent crystallinity for the inventive examples is generally higher than that of comparative monocatalyzed CAT1 interpolymers and substantially equivalent to that of comparative interpolymers monocatalyzed CAT2 interpolymers. Or at least, the crystallinity results of monocatalyzed CAT2 interpolymers vary widely.



While FIG. 5 shows that the Tg temperature of Inventive Example 13 is generally similar to that of monocatalyzed comparative interpolymer. But FIG. 6 show the Tg temperature range or width of Inventive Example 13 is substantially broader than comparative interpolymer. Fig. 7 shows that typical melt blends substantially approximate the Tg width of their respective component interpolymers. Since Inventive Example 13 would ordinarily be expected to follow melt blend results and performance attributes, the fact that the inventive product is characterized by (1) a single Tg peak having a shoulder rather than two separate and distinct peaks and (2) a substantially broader Tg width is a completely unexpected surprise.

We claim:

1. An interpolymer product comprising an  $\alpha$ -olefin  
interpolymerized with at least one vinyl or vinylidene  
aromatic monomer wherein the interpolymer product is  
5 characterized as having:

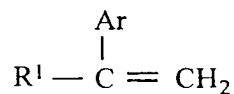
A) a melting point, as determined using  
differential scanning calorimetry, equal to or greater  
than the product of the equation:

melting point =  $128 - 1.3333 \times \text{total weight percent}$   
10 interpolymerized vinyl and/or vinylidene aromatic monomer,  
or

B) a glass transition temperature range or width at  
half peak temperature height of greater than or equal to  
15°C, preferably greater than or equal to 20°C, more  
15 preferably greater than or equal to 25°C, most preferably  
greater than or equal to 30°C, as determined using dynamic  
mechanical spectroscopy (DMS) loss modulus ( $G''$ ) data.

2. The interpolymer product of claim 1 wherein the  
20 product is a substantially random interpolymer comprising  
(1) from 27 to 46 mol percent of polymer units  
derived from

(i) the vinyl or vinylidene aromatic  
monomer represented by the following formula:

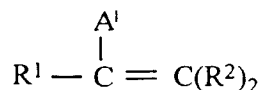


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wherein  $\text{R}^1$  is selected from the group of radicals  
consisting of hydrogen and alkyl radicals containing three  
carbons or less, and Ar is a phenyl group or a phenyl  
group substituted with from 1 to 5 substituents selected

from the group consisting of halo, C<sub>1-4</sub>-alkyl, and C<sub>1-4</sub>-haloalkyl; or

(ii) the hindered aliphatic or cycloaliphatic vinyl or vinylidene aromatic monomer is represented by the following general formula;



wherein A<sup>1</sup> is a sterically bulky, aliphatic or cycloaliphatic substituent of up to 20 carbons, R<sup>1</sup> is selected from the group of radicals consisting of hydrogen and alkyl radicals containing from 1 to 4 carbon atoms; each R<sup>2</sup> is independently selected from the group of radicals consisting of hydrogen and alkyl radicals containing from 1 to 4 carbon atoms; or alternatively R<sup>1</sup> and A<sup>1</sup> together form a ring system; and

(2) from 54 to 73 mol percent of polymer units derived from the α-olefin which comprises ethylene, or ethylene and at least one of propylene, 4-methyl-1-pentene, butene-1, hexene-1, heptene-1 or octene-1; or

3. The interpolymer product of claim 1 wherein the product is partially substantially random and partially random or alternating.

4. The interpolymer product of claim 2 wherein the substantially random interpolymer product is further characterized as pseudo-random.

5 5. The interpolymer product of claim 1 wherein the product is further characterized as being variably sequenced.

6. An interpolymer product comprising  $\alpha$ -olefin and  
10 at least one vinyl or vinylidene aromatic monomer made using at least two catalyst systems in at least one reaction environment or reactor wherein the catalyst systems are selected and operated to provide different monomer incorporation capabilities or reactivities.

15

7. The interpolymer product of claim 6 wherein at least one of the at least two catalyst systems is a constrained geometry catalyst system.

20 8. The interpolymer product of claim 6 wherein at least two of the at least two catalyst systems are constrained geometry catalyst systems.

9. The interpolymer product of claim 6 wherein all  
25 of the at least two catalyst systems are constrained geometry catalyst systems.

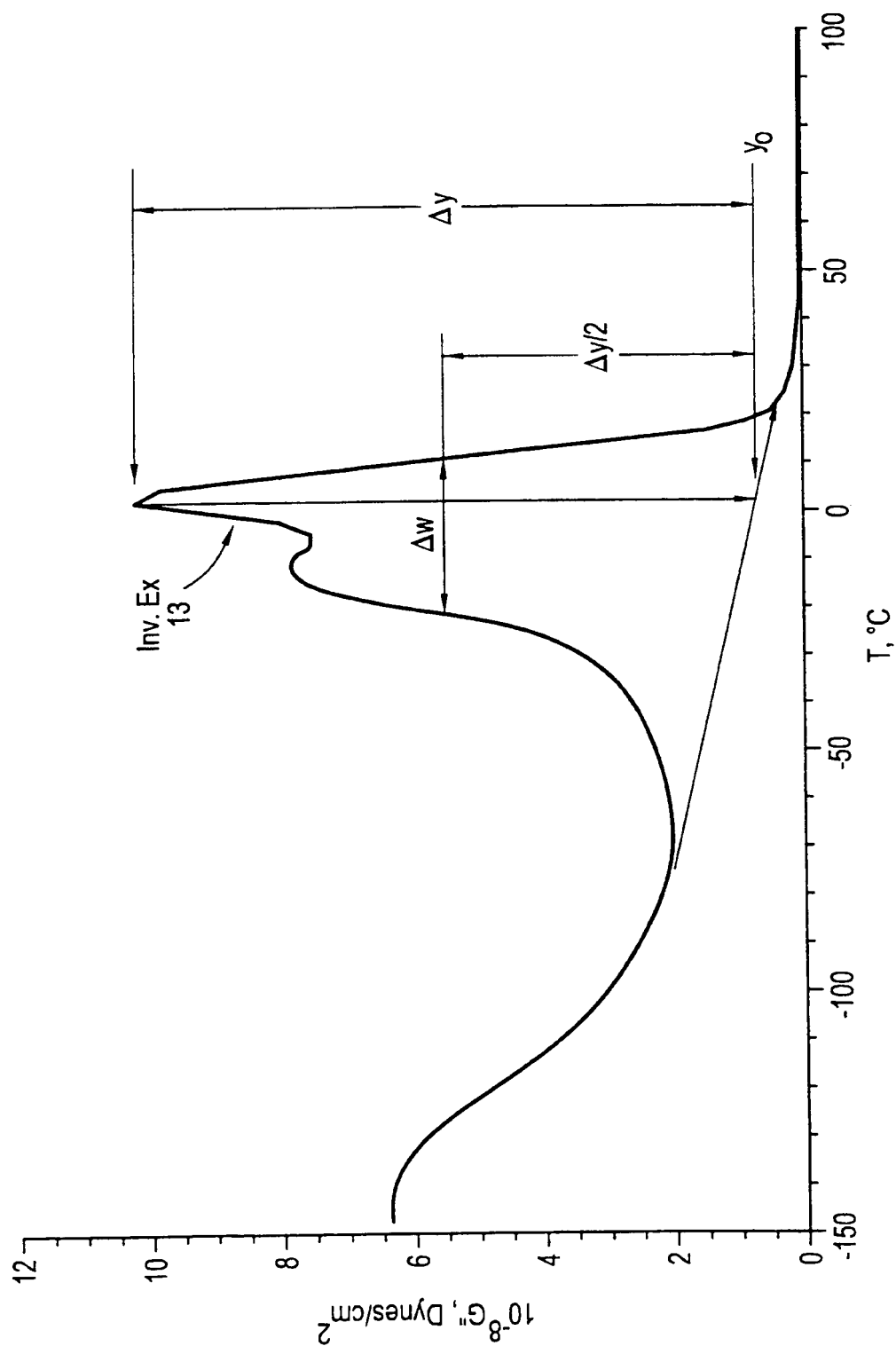
10. A process for making an interpolymer product, the product comprising an  $\alpha$ -olefin interpolymerized with

at least one vinyl or vinylidene aromatic monomer, the process comprising

- a) selecting at least two single site catalyst systems,
- 5       b) feeding the catalysts systems to at least one reaction environment or reactor, and
- c) controlling the reaction environment (or reactor), catalyst systems and interpolymerization conditions such that the catalyst systems operate or
- 10 function at different vinyl or vinylidene aromatic monomer incorporation capabilities or interpolymerization reactivity rates.

1 / 7

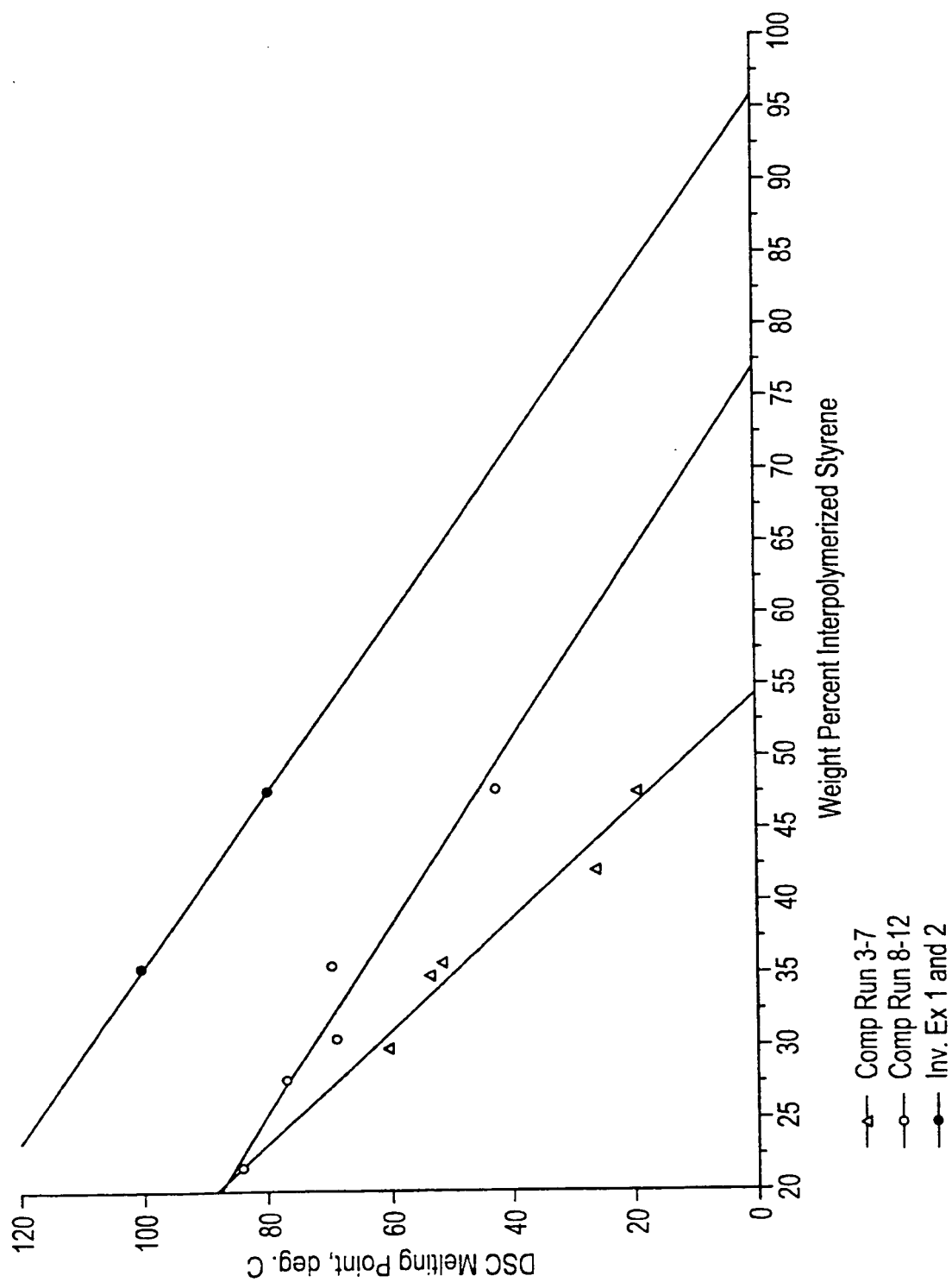
FIG. 1



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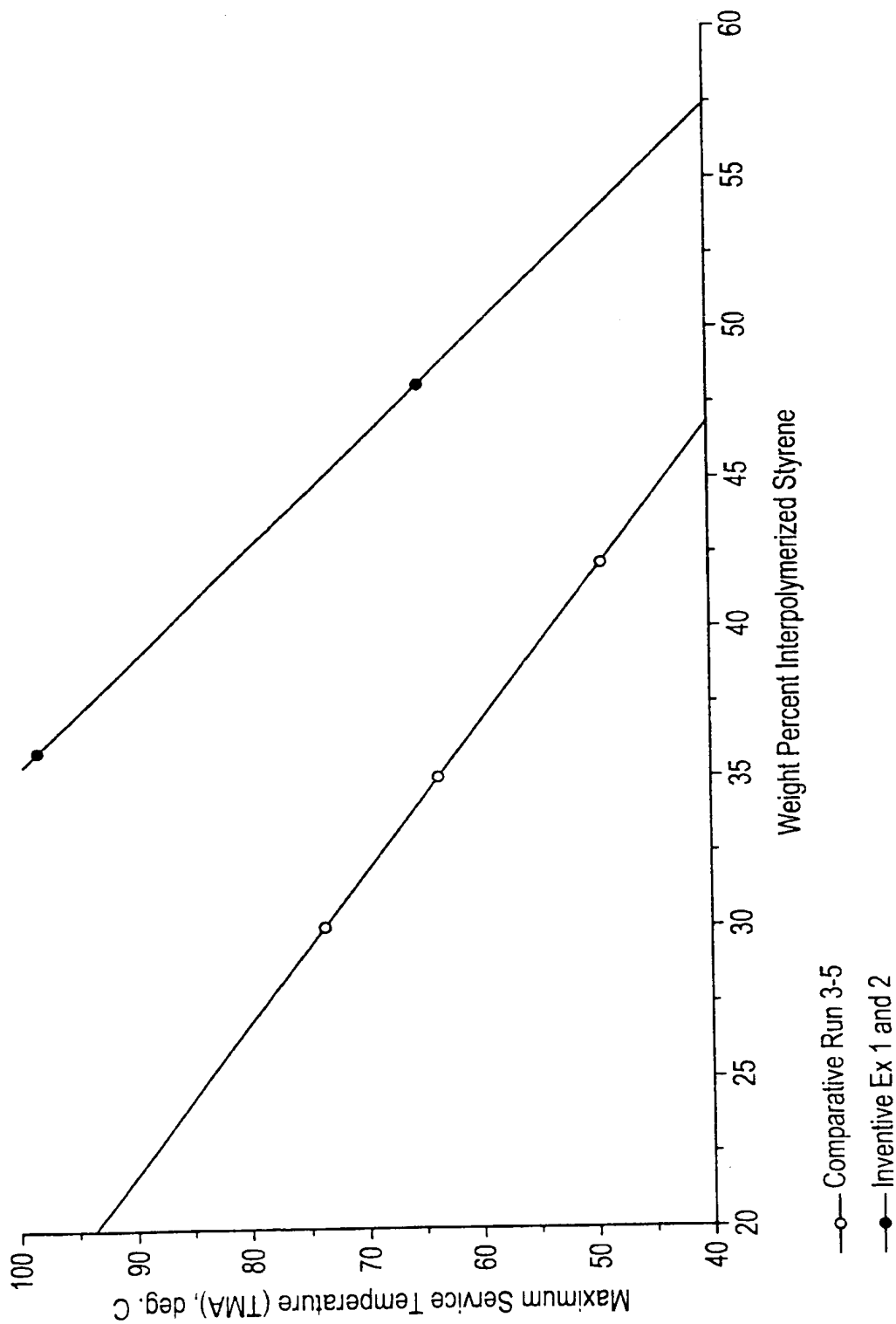
2 / 7

FIG. 2



3 / 7

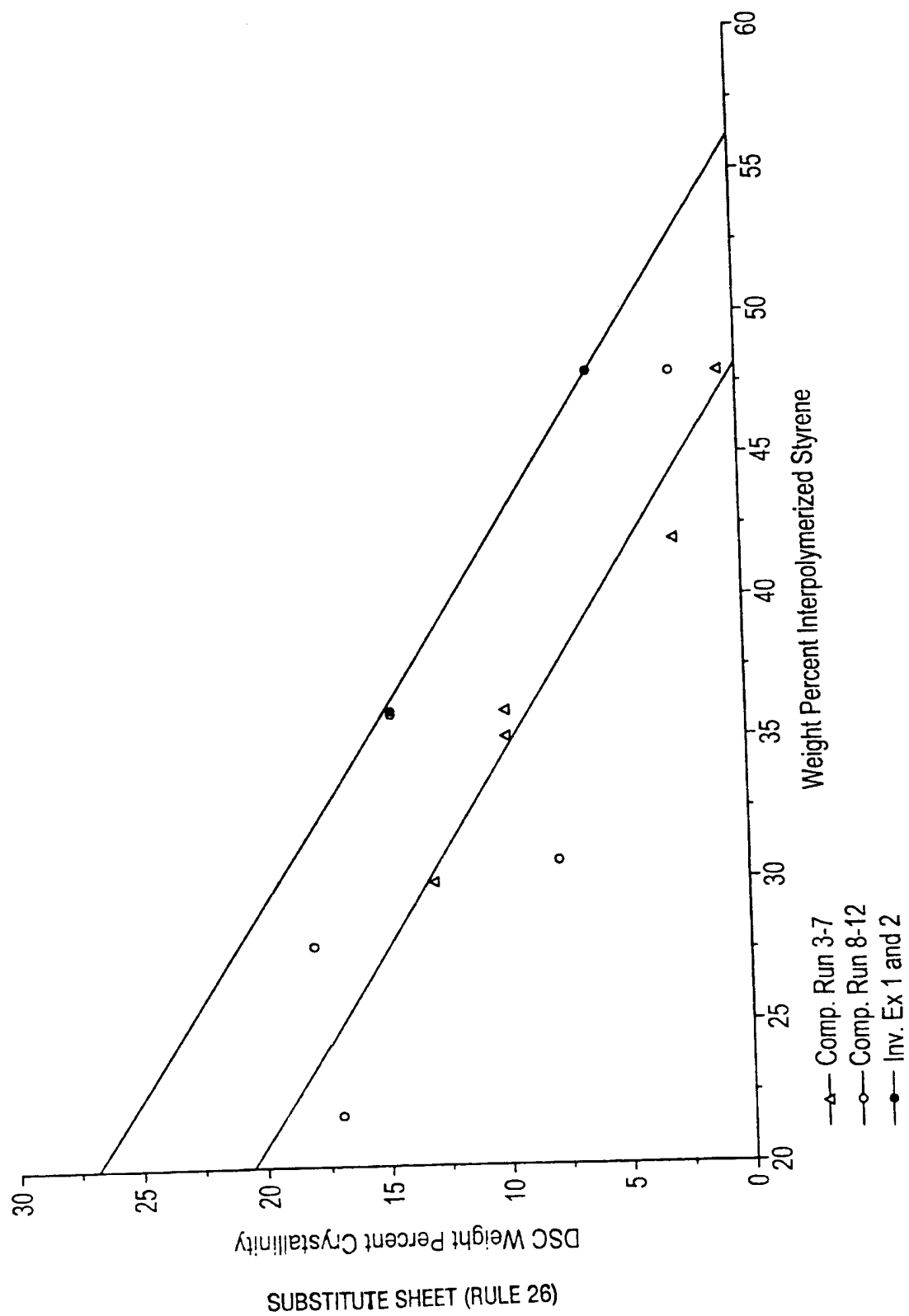
FIG. 3





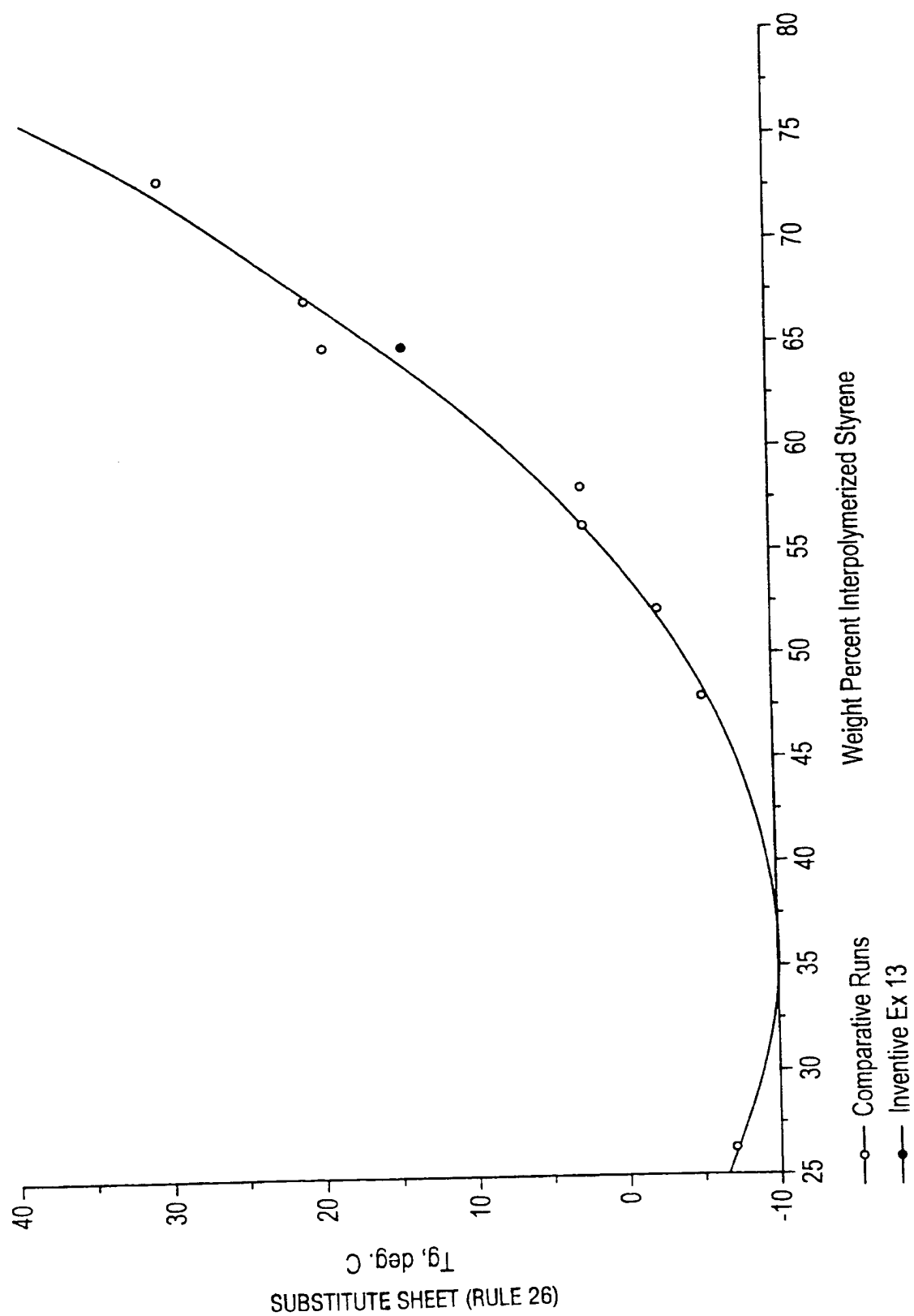
4 / 7

FIG. 4



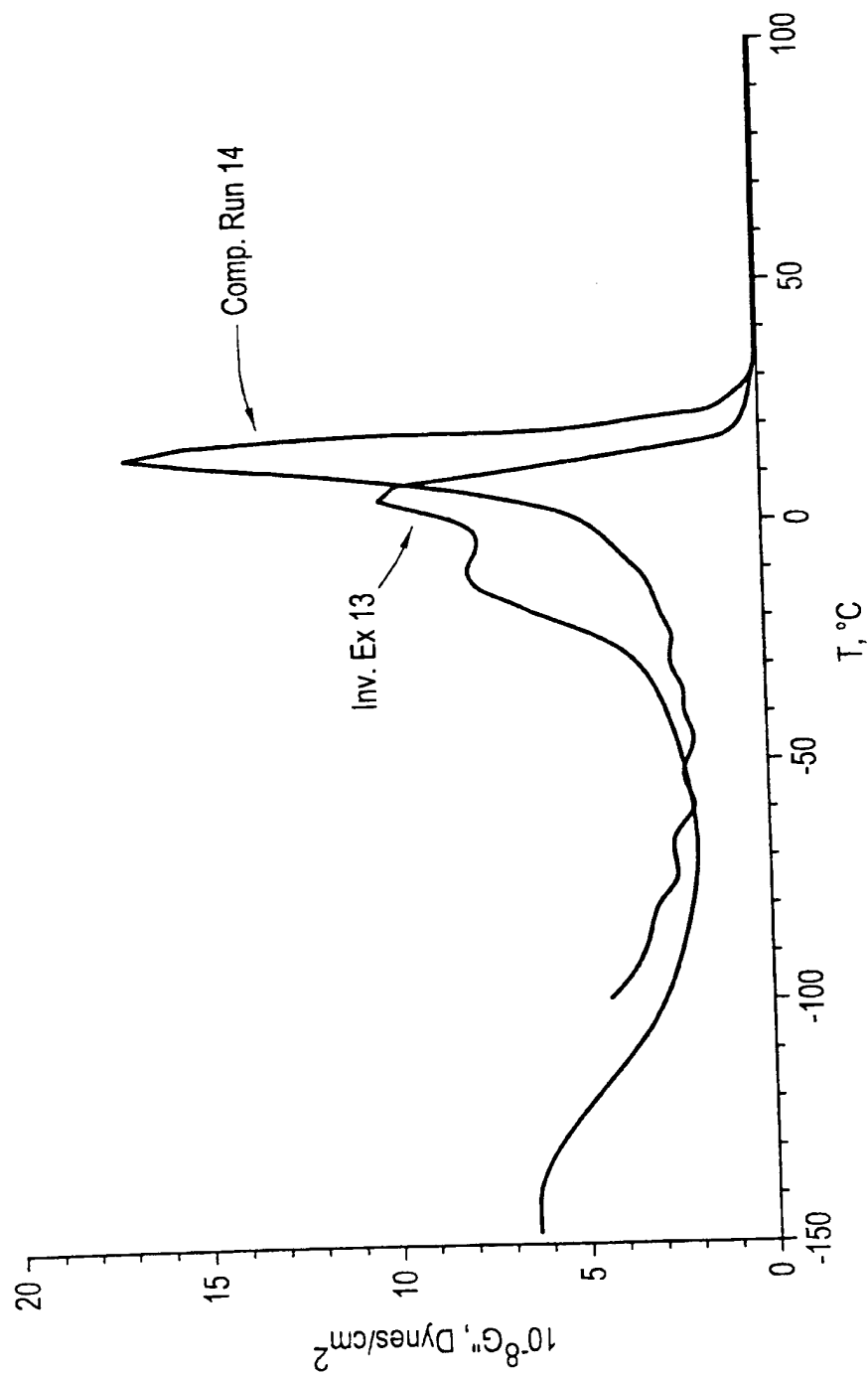
5 / 7

FIG. 5



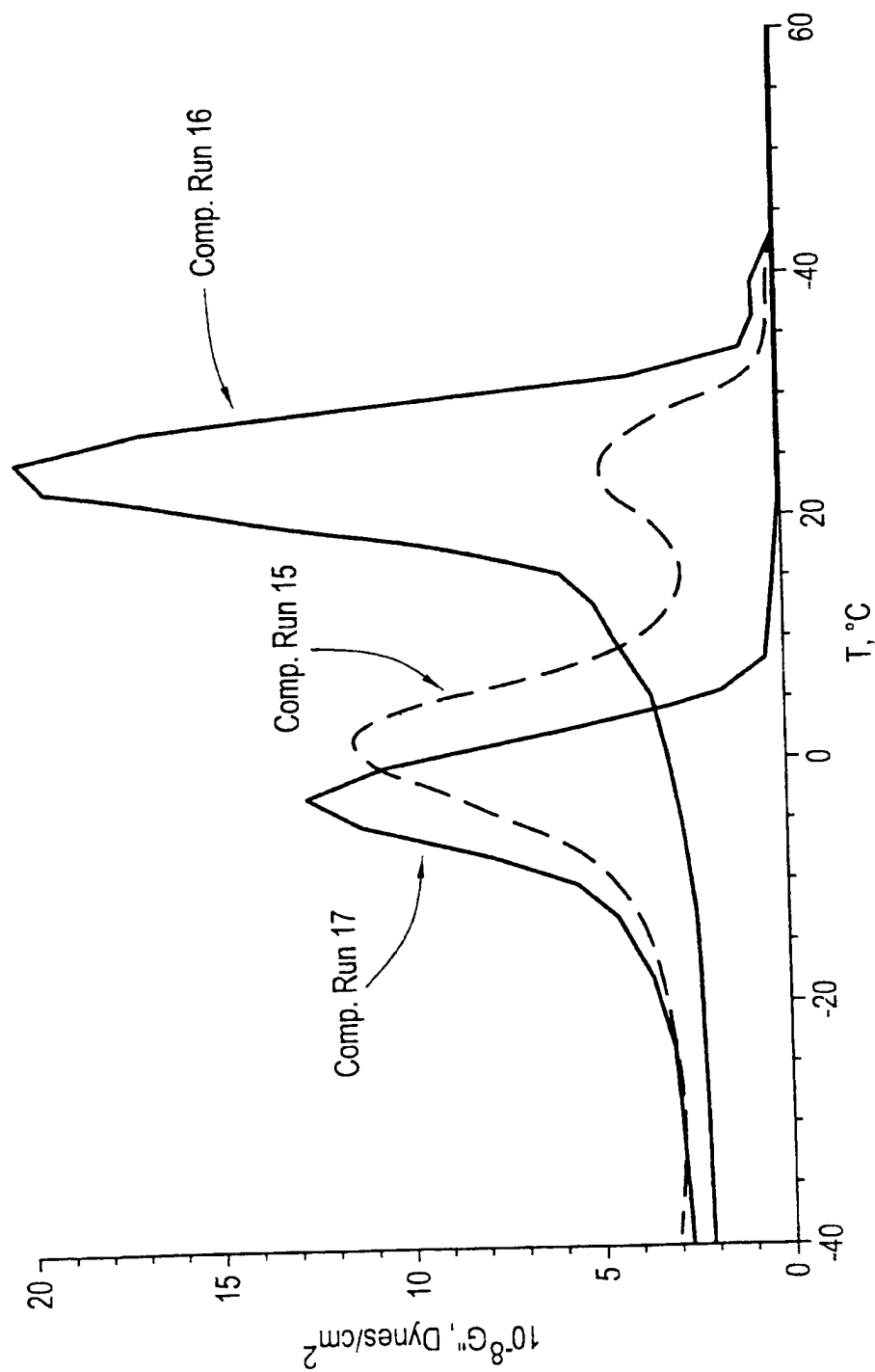
6 / 7

FIG. 6



7 / 7

FIG. 7



# INTERNATIONAL SEARCH REPORT

Int. l. Application No  
PCT/US 00/04121

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 7 C08F210/00 C08F210/02 //(C08F210/02,212:04)

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	DE 197 11 339 A (DENKI KAGAKU KOGYO KK) 30 October 1997 (1997-10-30) cited in the application claims; examples; tables 1,6	1
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

15 June 2000

Date of mailing of the international search report

28/06/2000

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# INTERNATIONAL SEARCH REPORT

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PCT/US 00/04121

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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